

Car and Parinello Molecular Dynamics
<http://www.cpmc.org/>

Basic tutorial to CPMD calculations

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CPMD basics

1.1 General ideas on the CPMD method

For details see references [1–3].

In the CPMD method the time-independent Schrodinger equation is not solved at each step, the main idea of the method is to transform the quantum adiabatic time-scale separation of fast electronic and slow nuclear motion into classical adiabatic energy-scale separation for the dynamics.

To achieve this goal the two component quantum / classical problem of First Principles (Ab-Initio) Molecular Dynamics (FPMD/AIMD), is transformed into a two component purely classical problem with 2 separate energy scales. The explicit time dependence of the quantum sub-system dynamics is also lost in the process. Furthermore since the kinetic evolution of the electronic structure is going to be considered apart from the one of the ions it is necessary to give a fictitious mass to the electronic degrees of freedom ($E_c = \frac{1}{2}mv^2$). Also, a term is added to the Hamiltonian of the system to ensure the adiabaticity of the relationship between the kinetic part from the ions and the one from the electrons/orbitals in other words there should be absolutely no exchange between the two kinetic parts.

In the program the word 'ELECTRONS' appears often for the keywords concerning the parametrization of the dynamics of the electronic sub-system, this terminology is not appropriate since the dynamical objects are actually the orbitals and not the electrons.

1.2 Structure of the CPMD input file

The CPMD input file is divided in sections, each of them contains specific keywords:

```
&SECTION
...
KEYWORD
comments
...
&END
```

The section named 'SECTION' start by `&SECTION` and end by `&END`. The CPMD code read keywords in capital letters, otherwise the text is considered as comments. Many sections can be used to create a CPMD input file (see the CPMD user manual for details) but only 4 sections are mandatory to run a CPMD calculation: CPMD, DFT, SYSTEM and ATOMS.

Because of their significant interest few additional sections are presented thereafter.

1.2.1 The INFO section

This section is used to present details about the calculation and the system under study. No keyword is required here, the information will simply be appended to the output file at runtime.

```
&INFO
  GeSe9, 480 atoms
  DFT-GGA-BLYP, FPMD ...
  or whatever information
  I want to use to describe
  what I am doing
&END
```

1.2.2 The CPMD section

This section is used to describe the calculation to be run.

```
&CPMD
  OPTIMIZE WAVEFUNCTION
  INITIALIZE WAVEFUNCTION ATOMS
  TIMESTEP
    3.0
  MAXITER (and/or MAXRUNTIME)
    50000
  PCG
  CONVERGENCE ORBITALS
    8.0E-06
  EMASS
    2000
&END
```

Many different type of calculation can be performed using the CPMD code, among others:

- OPTIMIZE WAVEFUNCTION
- OPTIMIZE GEOMETRY
- MOLECULAR DYNAMICS
- MOLECULAR DYNAMICS BO
- KOHN-SHAM ENERGIES
- PROPERTIES
- LINEAR RESPONSE
- EHERENFEST DYNAMICS
- TDDFT
- FREE ENERGY MD
- ...

many of them are briefly introduced in the next chapter (see Chap. [2]).

1.2.3 The DFT section

This section is used to describe the parameters of the Density Functional Theory (DFT).

```
&DFT
  FUNCTIONAL BLYP
  GC-CUTOFF
  0.1E-07
&END
```

And in particular the exchange-correlation functional (XC) to be used in the calculation, among: LDA, BP, BLYP, PBE, revPBE, XLYP, HCTH, OLYP ...

And Hybrid XC functional: B3LYP, PBE0, HSE06 ...

1.2.4 The VDW section

If required in the CPMD section of the input file:

1.2.4.1 Empirical VDW corrections

```
&CPMD
  ...
  VDW CORRECTION
  ...
&END
```

This section is used to describe how to treat Van Der Waals interactions:

```
&VDW
  EMPIRICAL CORRECTION
  VDW PARAMETERS
  ALL DFT-2
  S6GRIMME
  BLYP
  END EMPIRICAL CORRECTION
&END
```

1.2.4.2 Wannier VDW corrections

```
&CPMD
...
VDW WANNIER
...
&END
```

This section is used to describe how to treat Van Der Waals interactions:

```
&VDW
WANNIER CORRECTION
VERSION
  2
FRAGMENT BOND
  1.38
TOLERANCE WANNIER
  5.0
TOLERANCE REFERENCE
  1.0
PRINT INFO FRAGMENT
END WANNIER CORRECTION
&END
```

1.2.5 The PROP section

If the calculation described in the CPMD section of the input file is PROPERTIES:

```
&CPMD
PROPERTIES
WANNIER
...
&END
```

This section is used to provide details about the physical properties to be calculated.

```
&PROP
LOCALIZE
PROJECT WAVEFUNCTION
POPULATION ANALYSIS MULLIKEN
&END
```

1.2.6 The **SYSTEM** section

This section is used to describe the geometry of the system to be studied.

```
&SYSTEM
ANGSTROM
SYMMETRY
  1
CELL ABSOLUTE DEGREE
  10.00 10.00 10.00 90.00 90.00 90.00
CUTOFF
  100.0
KPOINTS MONKHORST-PACK
  2 2 1
&END
```

In this example:

- The **ANGSTROM** keyword specify that cell parameters (A, B and C) as well as atomic coordinates (see section [Sec. 1.2.7]) will be provided in Angstrom. **In the CPMD code the default unit for length and positions is atomic unit.**
- The **SYMMETRY** keyword + number on the following line, between 0 and 14, 0 = isolated system (molecule), 1 = cubic FCC ..., describes the symmetry.
- The **CELL** keyword specify that cells parameters and angles will be read on the next line (6 values).
- The **ABSOLUTE** keyword specify that cell parameters will be read in the format A, B and C. **The default format in CPMD is A, B/A and C/A.**
- The **DEGREE** keyword specify that cell angles will be provided in degrees for α , β and γ . **The default format in CPMD is $\cos\alpha$, $\cos\beta$ and $\cos\gamma$.**
- The **CUTOFF** keyword + value on the following line, specify the cutoff for the plane waves in Rydberg.
- The **K-points** (if needed only) in Monkhorst-Pack representation. Here $\mathbf{k}=2\times 1\times 1$

1.2.7 The ATOMS section

This section is used to give the atomic positions, it follows the structure:

```
&ATOMS

*PP_FILE_NAME.pps  PP_GENERATION_METHOD
  LMAX=P  LOC=P
  N_ATOMS
  x(1) y(1) z(1)
  x(2) y(2) z(2)
  ...
  x(N_ATOMS) y(N_ATOMS) z(N_ATOMS)

&END
```

The inner part being repeated as many times as the number of chemical species, ex:

```
&ATOMS
*GE-MT-BLYP.pps  KLEINMAN-BYLANDER
  LMAX=P  LOC=P
  1
  4.7367371096   6.6107492731   4.6811927823

*SE-MT-BLYP.pps  KLEINMAN-BYLANDER
  LMAX=P  LOC=P
  4
  -5.9669982281   -8.7467531007   11.2938278730
   1.8904372056  -10.8283093176   4.1633837562
   5.4988512174   4.9899517884   10.6568153345
   0.0059955793   -0.1450182640   4.3887246936

&END
```

This required to sort the atomic coordinates by chemical species.

1.2.7.1 Generate dummy atoms (e.g. the center of mass of the system)

```
&ATOMS
...
DUMMY ATOMS
1
TYPE2 2 1 2
&END
```

Only 1 dummy atom will be used, TYPE2 = center of mass (TYPE1 to TYPE4 available, see manual), and two atoms, number 1 and 2 are used. Negative numbers = all atoms to be used.

1.2.7.2 Impose constraints on atoms (Blue moon or fix atom positions)

```
&ATOMS
...
CONSTRAINTS
FIX STRUCTURE
1
DIST 1 2 7.200
FIX ATOMS
2
10 11
&END
```

With FIX STRUCTURE we fix the distance $|\mathbf{R}(1) - \mathbf{R}(2)|$ to 7.2 a.u. With FIX ATOMS we fix some atoms, here 2 atoms, number 10 and 11, and no force will act on these atoms.

Remarks

The section DFT describe the XC functional, other sections like VDW and ATOMS require keyword-/parameters sensitive to the XC functional chosen by the user in the DFT section. **Consistency in the choice of the XC functional in each of these sections is an absolute pre-requisite to any CPMD calculation.**

CPMD calculations

2.1 Wavefunction optimization

Before any molecular dynamics calculation it is mandatory to optimize the wavefunction of the system.

Since in the CPMD method the time-independent Schrodinger equation is not solved at each step it is mandatory to start the calculation with the best possible electronic structure, and thus the first step of any CPMD calculation is to optimize the wavefunction.

In the CPMD section add the keywords:

```
&CPMD
  OPTIMIZE WAVEFUNCTION
  INITIALIZE WAVEFUNCTION RANDOM
  TIMESTEP
    3.0
  MAXITER
    50000
  PCG
  CONVERGENCE ORBITALS
    8.0E-06
  EMASS
    2000
&END
```

- PCG = Use the preconditioned conjugate gradients for optimization, other are available: (O)DIIS, SD. **Be careful not to use multiple keywords !**
- CONVERGENCE ORBITALS = Convergence criteria, maximum value for the biggest element of the gradient of the wavefunction (default value = 10^{-5} a.u.).

- `MAXITER` = Maximum number of optimization steps (Default 10000), in the case of wavefunction optimization the keyword `MAXSTEP`, which is a parameter required for geometry optimization or molecular dynamics, can also be used.
- `WAVEFUNCTION` can also be initialized from the atom positions, then instead of `RANDOM` use `ATOMS` as keyword.
- `EMASS` = Fiction electron mass in a.u. (default value = 400 a.u.)

2.2 Geometry optimization

2.2.1 Using the `OPTIMIZE GEOMETRY` keywords = the automatic way

In the CPMD section add the keywords:

```
&CPMD
  OPTIMIZE GEOMETRY
  HESSIAN UNIT
  MAXSTEP
    50000
  CONVERGENCE GEOMETRY
    1.0E-04
  EMASS
    600
&END
```

The 'HESSIAN UNITS' keyword is required for the first run (if more than one are required), this is the initial approximate Hessian for geometry optimization. The optimize geometry routines in CPMD are automatic, the calculation will end when the atomic forces get lower than 10^{-4} a.u. (default is 5×10^{-4} a.u.), in other words when the energy will reach a minimum value and its derivative will become almost equal to zero.

It can work well, nevertheless if we start the calculation with a geometry too far from the real exact minimum then this minimum may be impossible to reach and the optimization will fail. To reach it, or at least to control the results obtained with this method it is possible to use the friction dynamics.

2.2.2 Using Molecular Dynamics + Friction forces = the manual way

In the CPMD section add the keywords:

```
&CPMD
MOLECULAR DYNAMICS
ANNEALING IONS
  0.9
TIMESTEP
  3.0
MAXSTEP
  50000
&END
```

Remarks

1. For both sections [Sec. 2.2.1 and 2.2.2] we can consider that the optimization is complete if the forces/gradients on X/Y/Z are $\leq 10^{-4}$. An example is presented in table [Tab. 2.1].

```
*****
*                                     *
*                               FINAL RESULTS                               *
*                                     *
*****

ATOM          COORDINATES          GRADIENTS (-FORCES)
1  C   8.4600   6.6095 11.2683   1.619E-04 -1.945E-04 -4.204E-04
2  C   9.7962  14.9558  9.0558   6.261E-05  3.067E-04  6.960E-05
3  H  11.3596  13.8968 10.0554   1.658E-04 -6.944E-05  8.040E-06
4  H   -1.1899 10.5870  9.5163  -2.748E-04 -5.825E-05 -3.162E-05
5  H   6.7304  6.0976 10.1723  -9.913E-05 -3.407E-04  3.046E-04
6  H   8.5220  8.7119 11.0357   2.546E-05 -2.293E-04  3.923E-04

*****
```

Table 2.1 *Typical output of a geometry optimization run in the CPMD code.*

2. If the fictitious mass of the electronic sub-system is too small or too big, then the frequencies arising from this mass will interfere with the energy minimization and the resulting energy will be too far from the Born-Oppenheimer, minimum energy, surface. This will result in more important vibrations around the total energy for the Hamiltonian \hat{H}_{EHAM} (which by construction has to be perfectly conserved) when running free dynamics.

2.3 Free CPMD dynamics

In the CPMD section add the keywords:

```
&CPMD
MOLECULAR DYNAMICS
TIMESTEP
  3.0
MAXSTEP
  50000
&END
```

In free dynamics the term E_{HAM} which describes the total energy from the Hamiltonian has to be perfectly conserved, therefore the initial electronic structure must be determined by optimizing the wave functions as shown in section [Sec. 2.1], otherwise E_{HAM} will not be conserved and the dynamics will be bad. See table [Tab. 2.2] for the typical output of a Car-Parrinello molecular dynamics run in the CPMD code.

| NFI | EKINC | TEMPP | EKS | ECLASSIC | EHAM | DIS | TCPU |
|-----|---------|-------|-----------|-----------|-----------|-----------|------|
| 1 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.515E-12 | 0.99 |
| 2 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.822E-11 | 0.96 |
| 3 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.414E-10 | 0.96 |
| 4 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.130E-09 | 0.96 |
| 5 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.316E-09 | 0.97 |
| 6 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.651E-09 | 0.96 |
| 7 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.120E-08 | 0.96 |
| 8 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.203E-08 | 0.95 |
| 9 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.322E-08 | 0.96 |
| 10 | 0.00000 | 0.0 | -13.12210 | -13.12210 | -13.12210 | 0.488E-08 | 0.96 |

- NFI: step number
- EKINC: kinetic energy of the fictitious electronic sub-system (a.u.)
- TEMPP: temperature of the system (K)
- EKS: Kohn-Sham energy (a.u.) (like potential energy in classical MD)
- ECLASSIC: EKS + Ionic Kinetic energy (a.u.)
- EHAM: $E_{\text{HAM}} = E_{\text{CLASSIC}} + E_{\text{KINC}}$, the conserved parameter in CPMD
- DIS: Mean square displacement of atoms since the first MD step (a.u.²)
- TCPU: CPU time for the corresponding MD step

Table 2.2 Typical output of a Car-Parrinello molecular dynamics run in the CPMD code.

Remarks

1. When changing the calculation from 'OPTIMIZE GEOMETRY' to 'MOLECULAR DYNAMICS' one must not use the velocities from the restart file.
2. In the output file labelled 'ENERGIES' the first column presents the kinetic energy of the fictitious electronic part. If the values in this column are too important and/or if they are subject to too much variation then there is a problem in the calculation.

2.4 Temperature control CPMD dynamics

In the CPMD section add the keywords:

```
&CPMD
MOLECULAR DYNAMICS
TIMESTEP
  3.0
MAXSTEP
  50000
TEMPCONTROL IONS
  800 100
&END
```

The first number is the target temperature, and the second is the tolerance around this value. Both are given in K. In this example the temperature of the system is to be oscillated around 800 +/- 100 K, if the temperature goes below 700 K or higher than 900 K then it is readjusted. Optional keywords for the fictitious electronic sub-system are:

```
&CPMD
TEMPCONTROL ELECTRONS
  0.04 0.01
&END
```

The first number is the target fictitious kinetic energy, and the second is the tolerance around this value. Both are given in atomic units.

2.5 Nosé thermostat

In the CPMD section add the keywords:

```
&CPMD
  MOLECULAR DYNAMICS
  TIMESTEP
    3.0
  MAXSTEP
    50000
  NOSE IONS
    1000 200
  NOSE ELECTRONS
    0.2 600
&END
```

In the first case (`IONS`) the first number represents the target thermodynamic temperature in K, the second the thermostat frequency in cm^{-1} . In the second case (`ELECTRONS`) the first number represents the target fictitious kinetic energy, the second the thermostat frequency in cm^{-1} . The value of the target fictitious kinetic energy has to be of the order of the value of the fictitious kinetic energy observed in a free-dynamics simulation (little bit higher is good).

When the Nosé thermostat is used, the frequency must be much higher for the `ELECTRONS` than for the `IONS`. The two Nosé thermostats (`IONS` and `ELECTRONS`) must be played on distinct frequencies yet leading to a similar thermalization for the two sub-systems, see chapter [Chap. 4] for details.

2.6 Electronic density of states

Note that several methods exist in order to achieve this calculation, two of these methods are introduced hereafter.

2.6.1 Kohn-Sham energies calculation

In the CPMD section add the keywords:

```
&CPMD
  ...
  RESTART WAVEFUNCTION COORDINATES LATEST
  KOHN-SHAM ENERGIES
    100
  ...
&END
```

The number that appears after the keyword `KOHN-SHAM ENERGIES` represents the number of unoccupied electronic states, this number depends on the system and has to be large enough so that the energy of the electronic states that surround the HOMO-LUMO gap are perfectly converged. This calculation can only be performed using a converged electronic structure, that is why one has to use a restart file (see section [Sec. 2.10] for detail) from a wave function optimization (see section [Sec. 2.1] for detail). Also worth to mention is the fact that this calculation requires significantly more memory than a standard CPMD calculation, both wavefunctions and Hamiltonian required to be stored in memory, the latest being diagonalized.

Van Der Walls interactions must be turned off for this calculation.

2.6.2 Free energy calculation

In the CPMD section add the keywords:

```
&CPMD
...
OPTIMIZE WAVEFUNCTIONS
FREE ENERGY FUNCTIONAL
INITIALIZE WAVEFUNCTIONS RANDOM
TROTTER FACTOR
0.001
BOGOLIUBOV CORRECTION
LANCZOS DIAGONALISATION
LANCZOS PARAMETERS n=5
1000 8 22 1.D-8
0.05 1.D-10
0.01 1.D-12
0.0025 1.D-15
0.001 1.D-17
ANDERSON MIXING=3
1. 0.1
0.01 0.1
0.005 0.1
TEMPERATURE ELECTRON
300.0
...
&END
```

The free functional calculation uses the Fermi-Dirac distribution in order to fill the electronic states as a function of the temperature. The first part of the calculation is a Born-Oppenheimer wave function optimization to calculate the electronic structure of the system. The parameters provided above likely depend on the system under study.

2.7 3D visualization of orbitals, electronic densities

The calculation and the extraction of the orbitals and densities is done using the CPMD code, afterwards the creation of the input files for 3D visualization is done using the CPMD2CUBE code.

2.7.1 CPMD keywords

In the CPMD section add the keywords:

```
&CPMD
...
RHOOUT BANDS
4
-805 -806 -807 -808
...
&END
```

Using the RHOOUT + BANDS keywords a certain number of bands or orbitals will be plotted. The number of orbitals is given in the second line, and their index, starting from 1, is given in the third line:

- *positive index* (ex: 806) = the electronic density is written, output files are stored in DENSITY.index, ex: DENSITY.806
- *negative index* (ex: -806) = the wavefunction is written, output files are stored in WAVEFUNCTION.index, ex: WAVEFUNCTION.806

2.7.2 CPMD2CUBE

The exact command depends on the nature of the object to be visualized:

- For a DENSITY:

```
./cpmd2cube.x -dens -centre DENSITY.806
```

- For a WAVEFUNCTION:

```
./cpmd2cube.x -wave -centre WAVEFUNCTION.806
```

It is also possible to use the `-inbox` keyword to force atoms to be put inside the simulation box when periodic boundary conditions are used.

2.8 Electron localization function ELF

The formalism of the electron localization function ELF [4–7] provides a deeper insight on the bonding localization. More precisely the ELF gives information on the degree of localization of the electronic density. When the ELF values are close to the maximum, it is possible to identify, for a given value, centers in space, so-called attractors, which are surrounded by disjoint ELF isosurfaces, so-called basins, defining different charge localization domains. Merging of different basins for slightly lower values of ELF may reveal the existence of localization domains having in common more than one attractor. This gives indications on the centers involved in the bonding and on the spatial extension of this latter. [8]

The calculation of the ELF requires to add a single keyword to the CPMD section of the input file, afterwards the creation of the input files for 3D visualization is done using the CPMD2CUBE code.

2.8.1 CPMD keywords

In the CPMD section add the keywords:

```
&CPMD
...
ELF
...
&END
```

At CPMD runtime this keyword will generate the creation of a file named `ELF` in the active directory.

2.8.2 CPMD2CUBE

The `ELF` file is a density file similar to the `DENSITY` files and has to be converted using the CPMD2CUBE code.

```
./cpmd2cube.x -dens -centre ELF
```

2.9 Maximally localized Wannier functions

2.9.1 CPMD keywords

In the CPMD section the calculation to be run must be changed to `PROPERTIES` followed by the `WANNIER` keyword, and some additional keywords to describe the details of the analysis:

```
&CPMD
  PROPERTIES
  WANNIER
  ...
  WANNIER WFNOUT ALL
  ...
&END
```

Then create a new properties "PROP" section that contains the following:

```
&PROP
  ...
  LOCALIZE
  ...
&END
```

This calculation will output in particular two files:

- `WANNIER_CENTER` that contains the positions of the Wannier centers
- `IONS+CENTERS.xyz` that contains the positions of both the Wannier centers and the atoms

2.9.2 CPMD2CUBE

The `WANNIER_?.?` file is a density file similar to the `DENSITY` files and has to be converted using the `CPMD2CUBE` code however the `'-dens'` keyword is not to be used:

```
./cpmd2cube.x -centre WANNIER_1.1
```

2.10 Restarts

In the CPMD section add the keywords:

```
&CPMD
...
RESTART WAVEFUNCTION COORDINATES VELOCITIES ACCUMULATORS LATEST
STORE
  50
RESTFILE
  2
...
&END
```

Optional keywords if Nosé thermostats are used:

```
&CPMD
...
RESTART ... NOSEE NOSEP LATEST
...
&END
```

With these keywords the calculation will be resumed with the information contained in a CPMD restart file which name is specified in the file LATEST, using the data regarding the WAVEFUNCTION, the atomic COORDINATES, the VELOCITIES and the ACCUMULATORS (ex: time step number, derivatives of many variables). The keyword ACCUMULATORS is interesting during a molecular dynamics, if the details of the calculation remain identical between each run.

If the temperature, the pressure, or else, changes then the keyword ACCUMULATORS must not be used.

In this case the RESTART files will be written alternatively every 50 steps, in this example 2 restart files will be written RESTART.1 and RESTART.2 (it can be more than 2 files) RESTART.1 will be written at 50, then RESTART.2 will be written at 100, then RESTART.1 will be re-written at 150 and so on ...

Controlling adiabaticity in CPMD

For details see references [1, 2, 9].

At this point a short introduction on the Car and Parrinello method is required.

3.1 Car-Parrinello equations of motion

Car and Parrinello postulated the following class of Lagrangians:

$$\mathcal{L}_{CP} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle}_{\text{Kinetic energies}} - \underbrace{\langle \Psi | \mathcal{H}_e | \Psi \rangle}_{\text{Potential energy}} + \underbrace{\text{constraints}}_{\text{To ensure orthonormality}} \quad (3.1)$$

The generic Car-Parrinello equations of motion are of the form:

$$M_I \ddot{\mathbf{R}}_I(t) = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi | \mathcal{H}_e | \Psi \rangle + \frac{\partial}{\partial \mathbf{R}_I} (\text{constraints}) \quad (3.2)$$

$$\mu_i \ddot{\psi}_i(t) = - \frac{\partial}{\partial \langle \psi_i |} \langle \Psi | \mathcal{H}_e | \Psi \rangle + \frac{\partial}{\partial \langle \psi_i |} (\text{constraints}) \quad (3.3)$$

Equations of motion [Eq. 3.2 and 3.3] refer respectively to the ionic and the fictitious electronic sub-systems. μ_i (μ) are the fictitious masses assigned to the electronic (orbitals) degrees of freedom.

According to the Car-Parrinello equations of motion, the nuclei evolve in time at a certain, instantaneous, temperature proportional to $\sum_I M_I \dot{\mathbf{R}}_I^2$. Following the same idea the fictitious electronic sub-system evolves in a fictitious temperature proportional to $\sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle$.

The 'fast fictitious electronic sub-system' must have a low fictitious electronic temperature ("cold electrons"), where as simultaneously the 'slow ionic sub-system' nuclei are kept at much higher temperature ("hot nuclei").

The fast electronic sub-system stays cold for long times but still follows the slow nuclear motion adiabatically. Adiabaticity means that the two sub-systems are decoupled, and that there is no

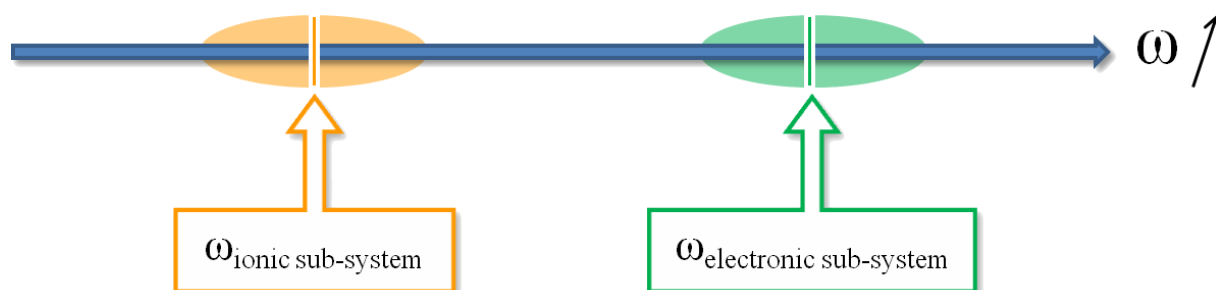


Figure 3.1 *Schematic representation of the vibration frequencies of the ionic and the electronic sub-system in CPMD. Electronic frequencies have to be higher than the ionic frequencies, and the two must not overlap.*

energy transfer between the two sub-systems in time. This is possible if the vibration spectra from both sub-systems do not overlap in their frequency domain so that energy transfers from the “hot nuclei” to the “cold electrons” become impossible on the relevant time scales, this is illustrated by a schematic in figure [Fig. 3.1].

3.2 How to control adiabaticity ?

The dynamics of Kohn-Sham orbitals can be described as a superposition of oscillations whose frequencies are given by:

$$\omega_{ij} = \sqrt{\frac{2(\epsilon_j - \epsilon_i)}{\mu}} \quad (3.4)$$

where ϵ_i is the KS eigenvalue of an empty (or occupied) state, μ is the fictitious mass parameter of the electronic sub-system.

It is possible to estimate the lowest frequency of the electronic sub-system, ω_e^{\min} :

$$\omega_e^{\min} \propto \sqrt{\frac{E_{gap}}{\mu}} \quad (3.5)$$

E_{gap} is the energy difference between the lowest unoccupied (LUMO) and the highest occupied (HOMO) orbital. ω_e^{\min} increases like the square root of E_{gap} and decrease similarly with μ .

Remark

The relations [Eq. 3.4 and 3.5] have the important consequence that it is not possible to study metals within the CPMD framework, since in that case no gap exists between the HOMO and LUMO !

To ensure the adiabaticity between the two sub-systems, the difference $\omega_e^{min} - \omega_i^{max}$ must be important, ω_i^{max} represents the highest ionic (phonon) frequency.

Since both E_{gap} and ω_i^{max} are quantities whose values are dictated by the physics of the system, the only parameter to control adiabaticity is the fictitious mass μ , therefore also called ‘‘adiabaticity parameter’’.

Furthermore the highest frequency of the electronic sub-system, ω_e^{max} , also depends on μ :

$$\omega_e^{max} \propto \sqrt{\frac{E_{cut}}{\mu}} \quad (3.6)$$

where E_{cut} is the largest kinetic energy of the wave-functions.

Therefore decreasing μ not only shifts the fictitious electronic frequencies upwards but also stretches the entire frequency spectrum.

Finally the molecular dynamics technique itself introduces a limitation in the decrease of μ due to the maximum time step Δt_{max} that can be used. The time step Δt_{max} is indeed inversely proportional to the highest electronic frequency in the system, which happens to be ω_e^{max} :

$$\Delta t_{max} \propto \frac{1}{\omega_e^{max}} \propto \sqrt{\frac{\mu}{E_{cut}}} \quad (3.7)$$

Equation [Eq. 3.7] thus governs the largest possible time step in a CPMD calculation.

The choice of the ‘‘adiabaticity parameter’’ is a compromise between equations [Eq. 3.5 and 3.7].

As illustrated in table [Tab. 2.2] in a CPMD calculation the quantities to follow and control are the kinetic energy of the electronic sub-system E_{KINC} , the potential energy from the Kohn-Sham equations E_{KS} , the classical first principles energy $E_{CLASSIC}$, and the conserved energetic quantity of the CPMD Hamiltonian E_{HAM} . Figure [Fig. 3.2] illustrates the evolution of these quantities during the dynamics and highlights the effect of the modification of μ and/or Δt_{max} on the evolution of $E_{CLASSIC}$ and E_{KINC} . $E_{HAM} = E_{CLASSIC} + E_{KINC}$, then if the variation on $E_{CLASSIC}$ are so important that E_{KINC} interferes with E_{KS} then there is no adiabaticity anymore.

Remark

E_{KINC} should be smaller than 20 % of the difference $E_{HAM} - E_{KS}$.

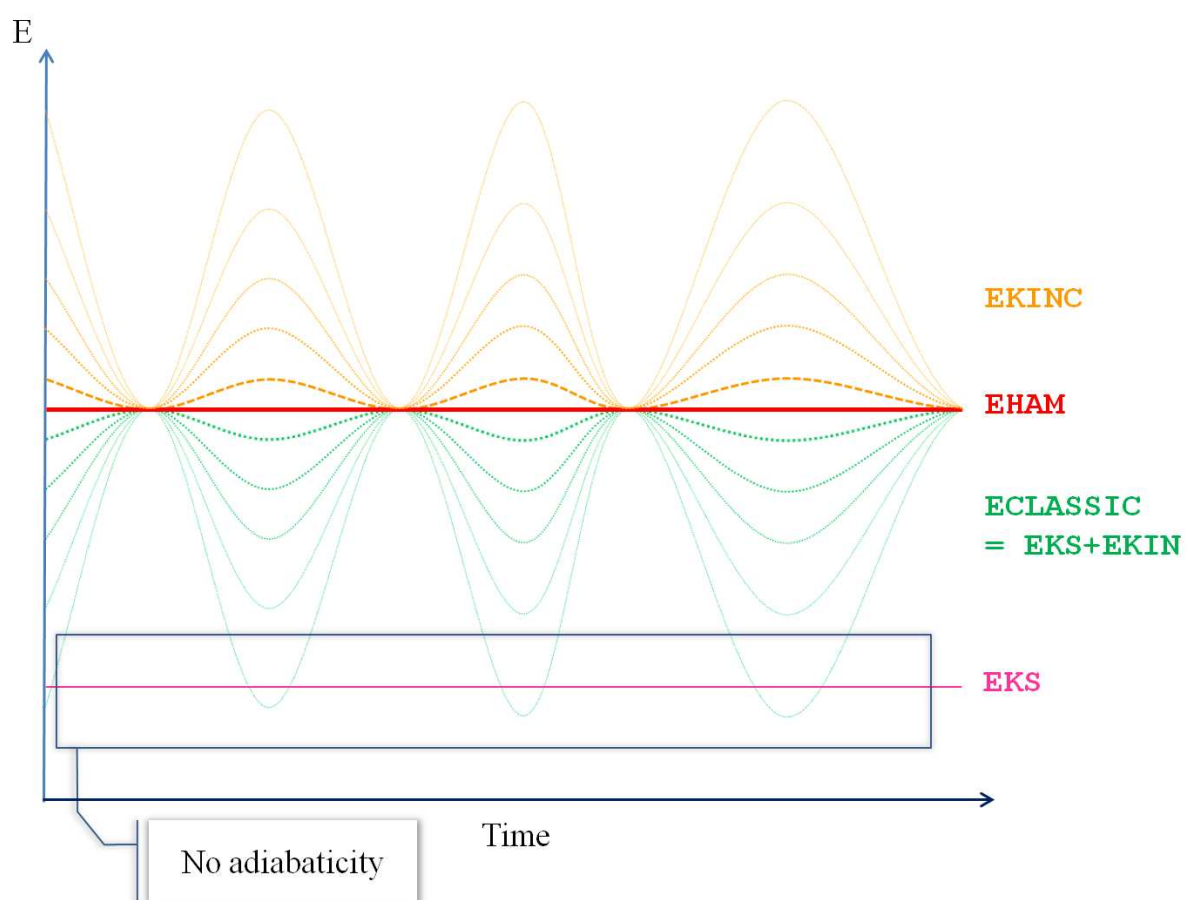


Figure 3.2 Schematic representation of the evolution of $EKINC$, EKS , $ECLASSIC$ and $EHAM$ during a CPMD calculation. The effect of the modification of μ and/or Δt_{max} is shown on the evolution of $ECLASSIC$ and $EKINC$.

Parameters of the Nosé thermostat

For details see references [10–13].

4.1 Nosé thermostats in the CPMD method

When introducing Nosé thermostats (on ions and/or fictitious electrons) the CPMD equations of motion [Eq. 3.2 and 3.3] are modified and friction terms are introduced to couple atoms and/or wave-function motions to the thermostats:

$$M_I \ddot{\mathbf{R}}_I(t) = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi | \mathcal{H}_e | \Psi \rangle + \frac{\partial}{\partial \mathbf{R}_I} (\text{constraints}) - M_I \dot{\mathbf{R}}_I \dot{x}_{\mathbf{R}} \quad (4.1)$$

$$\mu_i \ddot{\psi}_i(t) = - \frac{\partial}{\partial \langle \psi_i |} \langle \Psi | \mathcal{H}_e | \Psi \rangle + \frac{\partial}{\partial \langle \psi_i |} (\text{constraints}) - \mu \dot{\psi}_i \dot{x}_e \quad (4.2)$$

where the last term of each equation, $- M_I \dot{\mathbf{R}}_I \dot{x}_{\mathbf{R}}$ and $- \mu \dot{\psi}_i \dot{x}_e$, are friction terms that couple respectively atoms and wave-functions dynamics to the thermostats. These frictions terms are governed by the variable $x_{\mathbf{R}}$ and x_e which obey the following equations of motion:

$$Q_{\mathbf{R}} \ddot{x}_{\mathbf{R}} = 2 \left[\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - \frac{1}{2} g k_b T \right] \quad (4.3)$$

$$Q_e \ddot{x}_e = 2 \left[\sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle - E_{kin,e} \right] \quad (4.4)$$

where $\frac{1}{2} g k_b T$ is the average kinetic energy of the ionic sub-system, $g = 3N$ is the number of degrees of freedom for the atomic motion in a system with N atoms, k_b is the Boltzmann constant and T the physical temperature of the system. And $E_{kin,e}$ is the average kinetic energy of the fictitious electronic sub-system. The masses $Q_{\mathbf{R}}$ and Q_e determine the time scale of the thermal fluctuations of the thermostats.

4.2 Choosing the parameters

In a CPMD run controlled using Nosé thermostat(s), the physical temperature T is the most basic requirement for the thermostat that controls the ionic degrees of freedom. Then it is necessary to input the mass $Q_{\mathbf{R}}$ associated to this thermostat. Similarly when using a thermostat to control the fictitious electronic degrees of freedom it is required to input $E_{kin,e}$ and Q_e .

4.2.1 $E_{kin,e}$

A possibility to determine a value for $E_{kin,e}$ is to estimate the kinetic energy, $E_{kin,ad}$, related to the adiabatic motion of a model system of well known separated atoms. The adiabatic “atomic” wave-functions of this model follow the corresponding atom rigidly, thus it is possible to relate the kinetic energy to the velocities of the atoms:

$$E_{kin,ad} = 2 k_b T \frac{\mu}{M} \sum_i \langle \Psi_i | -\frac{1}{2} \nabla^2 | \Psi_i \rangle \quad (4.5)$$

M is the mass of one atom.

The value of $E_{kin,ad}$ gives a guideline for setting the average kinetic energy of the electronic wave-functions, since appropriate values of $E_{kin,e}$ have to be larger than $E_{kin,ad}$.

For $E_{kin,e}$ the recommended value is about twice $E_{kin,ad}$ [13].

4.2.2 $Q_{\mathbf{R}}$ and Q_e

The frequencies, $\omega_{T\mathbf{R}}$, of the thermal fluctuations associated to the thermostat that controls the ionic degrees of freedom are determined through:

$$\omega_{T\mathbf{R}} = \sqrt{\frac{2 g k_b T}{Q_{\mathbf{R}}}} \quad (4.6)$$

And for the frequencies, ω_{Te} , of the thermal fluctuations associated to the thermostat that controls fictitious electronic degrees of freedom through:

$$\omega_{Te} = \sqrt{\frac{4 E_{kin,e}}{Q_e}} \quad (4.7)$$

Basically the ionic and fake-electronic frequencies will decrease when increasing respectively $Q_{\mathbf{R}}$ and Q_e . The schematic in figure [Fig. 4.1] illustrates how the frequencies of the two thermostats should be set-up for a CPMD calculation.

- Frequencies of the thermostat coupled to the electronic sub-system must be lower than the frequencies of the electronic sub-system.
- Frequencies of the thermostat coupled to the ionic sub-system must be lower than the frequencies of the ionic sub-system.

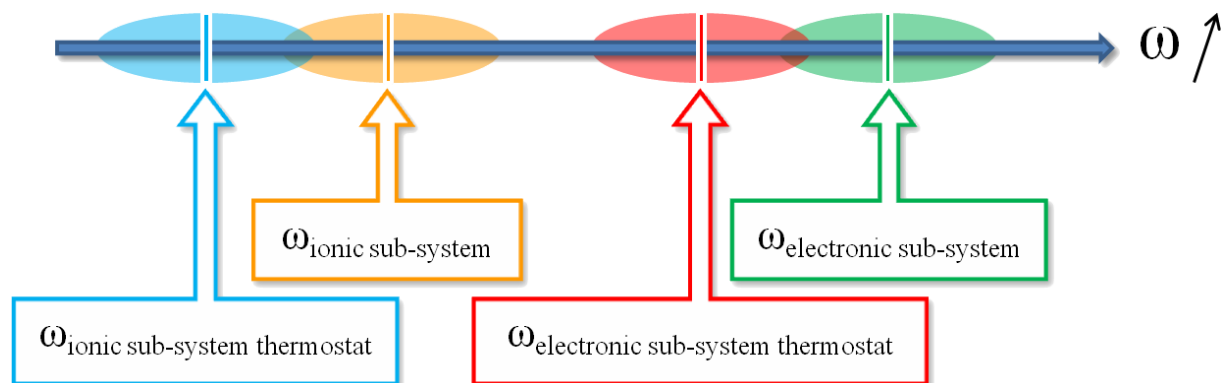


Figure 4.1 Schematic representation of the thermal frequencies of the ionic and the electronic sub-system, as well as the Nosé thermostats for both sub-systems in CPMD. Electronic frequencies (fictitious electrons + thermostat) have to be higher than the ionic frequencies (ions + thermostat), and the two sets of frequencies must not overlap.

- Electronic frequencies (fictitious electrons + thermostat) have to be higher than the ionic frequencies (ions + thermostat).
- Two sets of frequencies, electronic and ionic, must not overlap.

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